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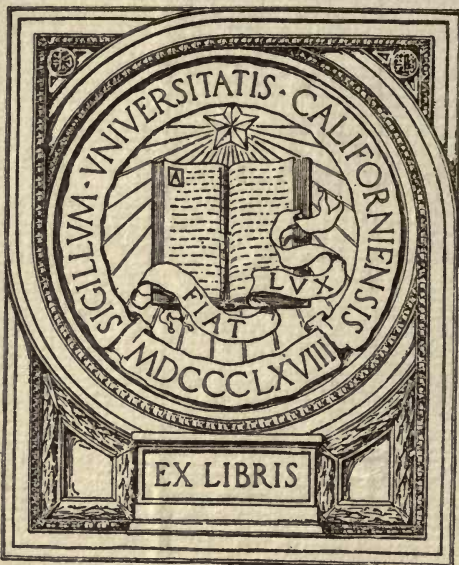
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Samuel L. Hoyt

**ON THE COPPER RICH KALCHOIDS**  
(COPPER-TIN-ZINC ALLOYS)





# ON THE COPPER RICH KALCHOIDS

Submitted in partial fulfillment of the requirements

of the

Degree of Doctor of Philosophy  
in the Faculty of Pure Science, Columbia University

by

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## Introduction

The plan of the present research was formulated at Columbia University after the suggestions of Dr. Campbell, director of the metallographical laboratory, and is intended to fulfil part requirements for the Ph. D. in that university. After the completion of the preliminary work at Columbia University, the research was transferred to the metallographical department of the "Eisenhüttenmännischen Instituts" at the Royal School of Technology, Charlottenburg, under the direction of Dr. Hanemann.

The constitution of the ternary alloys of copper, tin, and zinc up to about 50 per cent. zinc and 30 per cent. tin, has been studied both by thermal and micrographical analysis. The term "kalchoid" has been chosen to designate the ternary alloys of copper, tin, and zinc, as was first suggested by Thurston. This saves such names as brass and bronze for their more correct application and avoids confusion.

## On the Copper-Zinc System

Review of Literature. The first work of importance on the constitution of the brasses was published in 1896 by Charpy<sup>1)</sup> who studied the microstructure and mechanical properties of the commercial alloys up to about 50 per cent. zinc. He noticed the peculiar behavior of the  $\beta$  constituent in the 35 to 45 per cent. alloys and was inclined to consider this constituent amorphous, although he failed to recognise it under the guise of the coarsely crystalline alloys of 48 per cent. zinc. One interesting curve in connection with the influence of temperature on the tensile strength is given by Charpy,

<sup>1)</sup> Charpy, BullSocEnc 1 (1896) 180.

showing the sudden break in the curve which has more recently been studied in detail by English experimenters.

In the following year, Roberts-Austen published the first complete freezing point curve, along with the peritectic horizontals and a further line  $e''-e'$  called by him "eutectic"<sup>1)</sup>. The presence of this eutectic was immediately contested, Charpy in a second paper<sup>2)</sup> pointing to the fact that the ground mass, while undoubtedly finegrained, still failed to exhibit the characteristic structure to be expected, as in the case of the steels.

In 1904 Shepherd published the first complete constitution diagram, which is too well known to require especial discussion. He failed to find the line  $e'-e''$  of Roberts-Austen either pyrometrically or micrographically, and ascribed it to experimental error. Shepherd in discussing the solid solutions, refused to regard the composition with 60 per cent. zinc as a compound,  $Cu_2Zn_3$ , as is to be inferred however from the diagram. This phase is of great importance in the ternary alloys, and its behavior, as both solid solution and chemical compound, is not without significance.

In 1906 Guillet<sup>3)</sup> published some work on the brasses in connection with his investigation of the influence of the addition of tin to the brasses. This agrees with Shepherd's work and will be considered further on under the literature on the ternary alloys.

Then two other works appeared, both bringing additional evidence to support Shepherd in his diagram. Bengough and Hudson<sup>4)</sup> in their experiments on the heat treatment of Muntz metal and Tafel<sup>5)</sup> in his determination of the copper-zinc diagram, advanced microscopical and thermal evidence indicating that Roberts-Austen's line  $e'-e''$  was an error.

In a paper by Carpenter and Edwards<sup>6)</sup> presented to the Institute of Metals in 1911, the line  $e'-e''$  was again brought up. The authors (Carpenter and Edwards) sought to reestablish this line in the diagram chiefly by a series of very accurate curves covering the  $\beta$  range and supported by microphotographs. They drew attention to certain peculiarities in the alloys of this range which were readily ex-

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<sup>1)</sup> Roberts-Austen, Fourth Report to the Alloys Research Comm. (1897).

<sup>2)</sup> Charpy, BullSocEnc 2 (1897) 414.

<sup>3)</sup> Guillet, RevMétrg 111 (1906) 243.

<sup>4)</sup> Bengough and Hudson, JSocChemInd (1908) 43, 654.

<sup>5)</sup> Tafel, Metallurgie, Vol. V. (1908) 343.

<sup>6)</sup> Carpenter and Edwards, JInstMet 1 (1911).



plained on the assumption that such a line existed. In my opinion the curves offer very satisfactory evidence, but I shall attempt to show later on that the microphotograph given can hardly be accepted as exhibiting a duplex structure, as was stated in the above-mentioned paper.

To meet the criticism which this first paper called forth, Carpenter presented a second paper<sup>1)</sup> in which he described further experiments to prove the  $\beta \rightleftharpoons \alpha + \gamma$  inversion. He discussed annealing experiments on to different compositions near the eutectoid point, the one containing a slight excess of  $\alpha$ , the other a slight excess of  $\gamma$ . After several weeks of annealing at 445° C., a typical duplex structure was obtained, leaving no doubt as to the existence of the line  $e'-e''$  of Roberts-Austen.

In two more recent papers, Carpenter reported further work on the  $\beta \rightleftharpoons \alpha + \gamma$  inversion<sup>2)</sup>, dealing with the resolution of free  $\beta$  and the effect on this breakdown of the addition of third metals. In the first of these two papers, he gives a very interesting cooling curve showing rather conclusively that  $\alpha$  and  $\gamma$  do not reunite at some lower temperature to form perhaps a chemical compound, CuZn.

A study of the electrical conductivity of the brasses has been of great interest. In the  $\alpha$  field the results check very closely with the thermal and micrographical analyses, but as soon as the  $\beta$  field is entered we find a big discrepancy. The curve, instead of running linear from 37 per cent. zinc to 60 per cent. zinc, as would be expected from the diagram, runs linear to a maximum at about 49 per cent. zinc and again linear to about 59 per cent. zinc. From this it would seem that apparent  $\beta$  behaved under these conditions as a homogeneous solid solution. As above mentioned, a cooling shows that  $\alpha$  and  $\gamma$  evidently do not reunite; thus we have the paradox that  $\beta$ , though known to be heterogeneous, behaves as a homogeneous solid solution. This point awaits yet a satisfactory explanation<sup>3)</sup>.

Potential measurements, as well as chemical behavior have been used to study the constitution of the brasses<sup>4)</sup>, but little additional of a definite nature has been learned.

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<sup>1)</sup> Carpenter, *JInstMet* **2** (1912).

<sup>2)</sup> Carpenter, *JInstMet* **2** (1912) Vol. VIII.

<sup>3)</sup> See Guertler, *ZAnorgChem* **51** (1906) 397 and Luigi Norsa, *CR* **155** (1912) 348.

<sup>4)</sup> See for reference on "potential measurements", Laurie, *JChemSoc* **53** (1888) 104; Herskowitsch, *ZPhysChem* **27** (1898) 123; Puschin, *ZnorgChem* **56** (1907) p.1. For "chemical behavior": Lincoln, Klein and Howe, *JPhysChem* (1907) 501; Sackur, *Arb. k. Gesundheitsamt* **20** (1904) 512 and **22** 127.

**Experimental Work.** The copper-zinc alloys were made for the purpose of studying their microstructure, the  $\beta$  structural constituent in particular.

The concentrations examined ranged in composition from pure copper to 55% Zn. by weight. The microstructure, limits of saturation etc., check very closely with the results cited in the literature above. A detailed description of these alloys is therefore unnecessary. One point in particular which I wished to test was the stability of the  $\beta$  solid solution at normal temperatures. The only evidence which I had of a breakdown was in the cooling curves of Roberts-Austen. These cooling curves pointed to an eutectoid inversion corresponding to  $\beta \rightleftharpoons \alpha + \gamma$ . To test this point I took a cooling curve of an alloy with 48% Zn. It showed a heat effect at 455 degrees C. A heating curve of the same alloy showed a corresponding heat effect at 470 degrees C. This effect was recorded each time this range of temperature was passed through. Similar heating and cooling curves taken on a 5% alloy failed to show such a heat effect. This evidence, then, was considered to support that of Roberts-Austen, and a micrographical analysis was immediately taken up.

The alloys in the  $\beta$  range were examined under a very high power with lenses giving exceptional definition, to see if perhaps the heat effect noted on the cooling curves had given rise to a very fine heterogeneous structure invisible under the ordinary microscope. The  $\beta$  solid solution appeared in all cases to be homogeneous. Next the series of alloys was annealed at 450 degrees C for forty-eight hours continuously. The  $\beta$  solid solution appeared as before, homogeneous. To subject these alloys to further and more severe annealing, a mercury vapor bath was constructed. With this apparatus I hoped to be able to anneal for at least four weeks, an annealing which I considered to be very drastic. There was, however, one objection to this test: the temperature of the mercury vapor bath was approximately 100 degrees under the temperature of the heat effect observed. With careful manipulation, a constant temperature was easily maintained for any length of time, with but a very slight loss of mercury. The specimen was sealed in a glass tube, to protect it from the mercury, and annealed four weeks. Again, on examination, the  $\beta$  solid solution appeared homogeneous. It was at this point, when in search of another bath with which I could maintain a temperature closer to that of the heat effect, that I obtained a copy of Prof. Carpenter's first paper, referred to above. On receipt of this, I gave up further attempts to reveal the  $\beta$  inversion by micro-

graphical analysis. My conclusion was that the  $\beta$  solid solution, while undoubtedly having broken down into  $\alpha + \gamma$ , still, as a microscopical constituent behaved under normal conditions as a homogeneous solid solution. The microscopical constituent, Sorbite, of the medium carbon steels is very similar in appearance to the  $\beta$  solid solution and suggests itself immediately to one's mind. Whereas Sorbite is easily resolved into granular Pearlite, the  $\beta$  solid solution, as Carpenter has shown, is resolved into its constituents only with the most drastic annealing.

A further point which was noted is the similarity in appearance, under a high power, of the structures of the  $\alpha$  and  $\beta$  solid solutions. The rough appearance of such solid solutions, under a high power, renders it extremely difficult to distinguish between heterogeneous and homogeneous structures. A fine lamellar structure similar to that of Pearlite was noted in the alloys in the  $\alpha$  range.

### On the Copper-Tin System

Review of Literature. The freezing point curves of the Copper-Tin system appeared in the Fourth Report to the Alloys Research Committee, 1897. Campbell, in an Appendix to the Fifth Report (1901) pointed out the fact, for the first time, that the Copper-rich alloys underwent structural changes in the solid state. The first complete constitution diagram was than given by Heycock and Neville in 1903<sup>1</sup>).

Two other investigations followed, by Shepherd in 1906<sup>2</sup>) and Giolitti in 1909<sup>3</sup>).

The important points for the present are the limit of saturation of the  $\alpha$  solid solution, the temperature of the eutectoid inversion, and the composition of the eutectoid point. The limit of saturation varies from 5 per cent. in Giolitti's diagram to 13 per cent. in Shepherd's; while the eutectoid point remains more constant at 26 per cent. Its inversion temperature is given from 486 deg. to 500 deg. C.

In a very careful cooling curve taken by Heyn and Bauer<sup>4</sup>) on an alloy containing 83.5 per cent. copper, 16.0 per cent. tin, 0.2 per cent. zinc, with small amounts of arsenic and lead, this temperature is given as 525 deg. C. (See fig. 1.) This curve was recorded by taking the time  $\Delta t$  required for the alloy to cool an interval of 10

<sup>1</sup>) Heycock and Neville, *PhilTransRoySocLond* **202** (1903) 1.

<sup>2</sup>) Shepherd and Blough, *JPhysChem* **10** (1906) 515.

<sup>3</sup>) Giolitti and Tavanti, *GazChimIt* **38** (1909) 209.

<sup>4</sup>) Heyn and Bauer, *MittKMatPrüfAmt* **29** (1911).

deg. C. Measurement of the electrical potential has been used by Laurie<sup>1</sup>), Sackur and Pick<sup>2</sup>), Puschin<sup>3</sup>) and Ledoux<sup>4</sup>), to study the composition of the bronzes. This work has shown that the constituent  $\delta$  is a solid solution, and not the compound  $\text{Cu}_4\text{Sn}$ ; further the existence of the compound  $\text{Cu}_3\text{Sn}$  was established. These results were also confirmed by Guertler's work on the electrical conductivity of metallic alloys<sup>5</sup>).

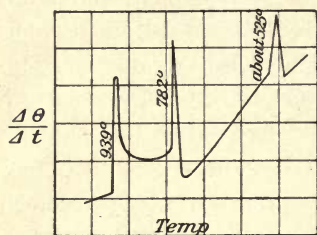


Fig. 1.

Experimental Work. The copper-tin alloys were made up for the purpose of examining their microstructure, locating the

limit of saturation of the  $\alpha$  solid solution, and studying the eutectoid inversion of the  $\beta$  solid solution.

A review of the literature on the Copper-Tin System revealed two discrepancies in the results of the various experimenters; one, the limit of saturation of the  $\alpha$  solid solution, and, second, the temperature of the eutectoid inversion. The limit of saturation of the  $\alpha$  solid solution seems to depend entirely on the rate of cooling, in other words, the eutectoid may enter on account of the inhomogeneity of the alloy. Guertler<sup>6</sup>) states that on ordinary rates of cooling, a second constituent may be seen in an alloy of 2 At. per cent., due to the zonal dendritic structure. This was confirmed in the present research. It then became necessary, when speaking of limits of saturation, to refer to certain standard rates of cooling and in comparison to always use the same rate as a standard. Annealing at 550 degrees C., with subsequent slow cooling, shifted the apparent limit of saturation to approximately 10% tin. It is to be noted that a temperature above that of the eutectoid inversion was chosen so that the eutectoid formed on this occasion in the same manner as before. To test the second point, the temperatures of the eutectoid inversion, heating and cooling curves of an alloy with 26% tin, were taken. A well defined heat effect was recorded at the mean temperature of 525 degrees C., checking very closely with the cooling curve of Heyn's. On no occasion was

<sup>1</sup>) Laurie, JChemSoc 53 (1888) 104.

<sup>2</sup>) Sackur and Pick, ZAnorgChem 58 (1908) 46.

<sup>3</sup>) Puschin, ZAnorgChem 56 (1907) 1.

<sup>4</sup>) Ledoux, CR 155 (1912) 35.

<sup>5</sup>) Guertler, ZAnorgChem 51 (1906) 397.

<sup>6</sup>) Guertler, Metallographie I 1 668.

this heat effect recorded at a temperature under 500 degrees, which was very difficult to reconcile with the results as given by former experimenters. As a result of this preliminary work, the limit of the  $\alpha$  solid solution was taken as 10%, and the eutectoid temperature as 525 degrees C.

### On the Copper-Tin-Zinc System

Review of Literature. Except for the work of Thurston on the mechanical properties of the kalchoids<sup>1)</sup>, there has been no systematic research covering the entire range of the commercially important copper-rich ternary alloys. There has, however, been considerable work done in single branches on physical and chemical measurements, and the influence of tin on the mechanical properties and microstructure of the brasses. Although the work of Thurston offers considerable matter of a speculative nature on the constitution of the kalchoids, still, since it deals mainly with the mechanical properties, it (and other similar work) will not be considered here.

Guillet<sup>2)</sup> in 1906 published a series of experiments on the mechanical properties and microstructure of the kalchoids up to about ten per cent. tin. It is interesting to note that in his microphotographs evidence pointing to the eutectoid inversion is given in the appearance of the eutectoid upon the addition of about three per cent. tin to the 30 per cent. brass, which point, however, seemed to escape his notice. But the presence of a "constituant spécial" in the microstructure of the alloys with more tin did attract his attention. This "special constituent" was observed if tin was added directly to  $\alpha + \beta$ , when the tin content exceeded a certain amount, depending on the zinc content.

On adding tin to  $\alpha + \beta$ , the tin was considered first to enter the  $\alpha$  up to 0.7 per cent. tin, and then to enter the  $\beta$ . Any excess formed the "special constituent". (This special constituent observed by Guillet will be seen later — under the discussion of the microstructure — to be the  $\gamma$  solid solution; and the irregularities he notes in this field will be seen to be due to the influence of tin on the eutectoid inversion.) It was in this field, just off the  $\alpha + \beta$  range, that a remarkable improvement in the properties was noticed. This, Guillet attributed as due to the "special constituent", which conclusion, the author believes should not necessarily follow. I hold rather to the opinion that the

<sup>1)</sup> Thurston, Materials of Engineering, vol. III.

<sup>2)</sup> Guillet, RevMétrg 3 (1906) 243.

rapid rise in properties is due to the tin going into apparent solution, without forming the special constituent.

Miller<sup>1)</sup> in a series of experiments testing the influence of various metallic and nonmetallic elements on the properties of normal statuary bronze, determined the melting points of ten copper-rich kalchoids, which were used for comparison in the construction of the ternary diagram. Nothing of their microstructure was noted by him, as the constitution of these ternary alloys was at that time not understood.

Johnson<sup>2)</sup>, in a paper before the Institute of Metals, discussed the influence of tin on the microstructure of the brasses. He seemed inclined to discredit the theory advanced by Guillet, in that he considered the eutectoid structure due to the formation of the compound  $\text{Cu}_4\text{Sn}$ , which gave the customary eutectoid of the copper-tin series. Considerable stress was laid on the importance of the influence of tin on brass, but nothing conclusive could be offered at that time.

As mentioned above, Carpenter read a paper on the effect produced by the addition of third metals to the pure structurally free  $\beta$ . In this the influence of tin was discussed, with the conclusion that 0.995 per cent. tin caused the resolution, so that it was visible under 150 diameters, — an accompanying microphotograph<sup>3)</sup> being cited as evidence. It will be seen later that the case is hardly so simple as it appears from this paper; and indeed, in my opinion, Professor Carpenter's microphotograph does not show the eutectoid structure. If the eutectoid structure is present, it can be and should be, I believe, clearly and undeniably shown. Figures 35a, 35b and 36 of the present paper show the desirability of correlating high and low magnifications for the sake of illustrating such a point.

Experimental Work. The metals used for this research were electrolytic copper practically pure, and Kahlbaum's best grades of tin and zinc. The melts were made up to weigh approximately 50 or 100 grams, the latter in case the cooling curves were to be taken. For preparing the alloys two furnaces were used. That employed in case the melts were to be cast (chill cast in an iron mold), was constructed in the laboratory: a small gas-fired furnace with blast, in which a temperature of 1200 deg. C. could be easily maintained. The other, a large natural draught gas furnace — giving fairly good insulation

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<sup>1)</sup> Miller, *Metrg* 9 (1912) 63.

<sup>2)</sup> Johnson, *JInstMet* 1 (1912), vol. 7.

<sup>3)</sup> Carpenter, *JInstMet* 2 (1912), vol 8, Pl. XVI, 7.

but at the same time handy to work with — was used in case cooling curves were to be taken. Special attention was paid to keeping the temperature carefully regulated, especially in preparing the 100 gram alloys. No uncommon difficulties arose, both furnaces working satisfactorily. Hessian crucibles were used. As a guard against oxydation, a cover of borax (or of finely ground carbon which was used in the large furnace) gave very good results — the one disadvantage of the borax cover being that the borax attacked the walls of the crucible and also took up copper from the melt. The 50 gram melts, after preparation were either allowed to cool in the furnace, or, in order to produce a fine grained structure, were chill cast in an iron mold; while in the case of the 100 gram alloys, ther thermo-element was inserted into the melt and it's cooling curve taken direct.

It was mentioned above that in case borax was used as a cover, copper was taken up out of the melt. This arose chiefly from the necessity of melting at least part of the copper before adding the cover. Thus the copper became oxidized and was readily absorbed by the borax. This resulted in a variable loss of copper.

It was considered necessary to analyze the 50 gram alloys, and throughout the following method was employed. First, the tin was removed by dissolving one gram of the alloy in concentrated nitric acid, and filtering the tin off as meta-stannic acid. The copper in the filtrate was determined by the iodine and thiosulphate method described in the Journal of the American Chemical Society for Dec. 1911. In this method the nitric acid is destroyed by sodium hypo-chlorite, The following solutions were used: (1) Sodium-hypochlorite, made by boiling 112 grams calcium hypo-chlorite with 100 grams anhydrous sodium carbonate in 1200 cubic centimeters water and filtering; (2) a 5 per cent. solution of phenol; (3) sodium hydrate 20 per cent.; (4) acetic acid 50 per cent.; (5) potassium iodide 30 grams per 100 cubic centimeters; (6) sodium thiosulphate for titration; (7) starch indicator. The determination was carried on in this order: (1) pipette off 50 centimeters of the filtrate (made up to 250 cc.) into a 300 cc. Erlenmeyer flask, and add from two to four cc. of the hypochlorite (or until the green color appears and chlorine gas is given off); (2) add ten cc. of phenol to take up the chlorine, blowing out any remaining; (3) add sodium hydrate until a slight precipitate forms (add immediately otherwise nitrophenol forms); (4) add acetic acid till precipitate disappears; (5) titrate for copper with sodium thiosulphate as usual. The zinc is taken as the difference.

To determine the composition of the 100 gram alloys used for the cooling curves, the method of weighing before and after preparation was employed.

To test the accuracy of this method, pure copper-tin alloys with a known amount of copper and tin were made up, proceeding in the usual manner. The alloys on being weighed, after preparation, had lost no weight. Likewise copper-tin-zinc alloys, allowing for approximately 2.5 to 4 per cent. Zinc loss, depending upon the composition, were made up. The weight of the alloys in this case varied but  $\frac{1}{2}$  one of per cent. from 100 grams, the weight desired.

Loss in weight was attributed to zinc volatilization; but whenever excessive loss in weight, inhomogeneity, or the like, gave rise to any doubt, the melt was laid aside and not used.

Certain of the alloys were subjected to annealing, which was usually carried on in an ordinary Heraeus furnace, the specimens being sealed in an iron pipe to prevent oxidation. The time of annealing averaged about 48 hours, the current being taken from a storage battery for overnight work.

For etching, two reagents were used, basic cuprous chloride and acid ferric chloride. These reagents work in like manner attacking the copper-rich constituent first and leaving the  $\gamma$  a bright gray. The basic cuprous chloride is preferable for the zinc-rich alloys, the acid ferric chloride for the tin-rich alloys.

In making the thermal analysis (1) the  $\frac{\Delta t}{\Delta \theta}$  method was employed when a complete cooling curve was taken; (2) the  $\frac{\Delta(\theta - \theta')}{\Delta \theta}$  method, when transformations in the solid state were to be definitely located. Under the first method, intervals in time were recorded by a Richardson chronograph. After considerable unsatisfactory experimenting with the platinum element, other elements were tried, and finally one of nickel wire and constantin wire of 6 millimeters diameter was found to be most suitable, and was employed in all subsequent work. This element remains exceptionally constant under varying conditions and has a very high thermo-electric force such that with a resistance of 1200 Ohms (including the resistance of the galvanometer) 1 millivolt is equal to only about 33 degrees C. On continued heating, the nickel wire becomes brittle and the element must be frequently replaced; however this counts as a very small item against it, when we take into consideration its cheapness. The compensation element was made of



two pieces of constantin wire connected by a 5 centimetre piece of nickel wire. Electrolytic copper was used as the neutral body. All work was done in an atmosphere of illuminating gas.

The ternary diagram. The ternary alloys were chosen in order to study the constitution of those copper-rich alloys within the commercial range. Although the diagram (Fig. 5), has been drawn complete, the dotted lines are to be regarded as constructed on purely theoretical grounds. The liquidus surface consists of two parts (that is, up to 30 per cent. tin and 50 per cent. zinc) corresponding to the equilibria  $\alpha + \text{liquid}$  and  $\beta + \text{liquid}$ . The line between the  $\alpha$  and  $\beta$  surfaces was determined by noting at what compositions the peritectic point disappeared; but this same line for the  $\beta$  and  $\gamma$  surfaces is purely theoretical. That the  $\alpha$  surface extends far out into the diagram — considerably further than one might expect — is from the thermal evidence unmistakable. The temperatures of the liquidus surfaces are shown by the contour lines. The solidus surfaces run under the liquidus surfaces in the same manner in which the solidus lines follow their coordinate liquidi in the two binary systems. We have two surfaces which correspond to the separation of the  $\alpha$  and  $\beta$  solid solutions from their melts, viz, the planes 1—4—4, and 5—5—10—10 in Figure 2. These surfaces are connected by the peritectic surface 4—4—2—2. The line 5—5, called “maximum peritectic” (Fig. 5), was drawn to show about where the corresponding points in the binary systems would come in the ternary diagram. On the copper side of this line, the alloy going solid with the peritectic reaction  $\alpha + \text{liquid} \rightleftharpoons \beta$ , the cooling curves show a sharp return from the peritectic maximum: while on the other side, as the alloy still remains part liquid ( $\beta + \text{liquid}$ ), the cooling curves exhibit a much slower return, corresponding to the freezing of the remaining liquid. The other part of the peritectic surface extends up to the line 2—2. A second peritectic surface runs from 10—10 to 3—3, at which temperature  $\beta$  reacts with the melt. This is clearly to be seen on the cooling curve. The evidence is not sufficient to locate these lines absolutely. Between the lines 5—5 and 10—10, the alloys solidify as a series of solid solutions according to the reaction  $\beta + \text{liquid} = \beta$  — to be seen on examining the cooling curves.

Since we find no fundamental difference in the behavior of the ternary alloys, on solidifying, from that of the binary alloys, the ternary alloys may be termed “pseudo binary”. Following the lines through the system as indicated, the process of solidification of any alloy may be seen at a glance, and at the same time be compared to that of any

corresponding alloy, or, better expressed, group of alloys of either the copper-tin or copper-zinc series (see Figures 2 and 4). For example, the ternary alloys within the area 1—4—4 solidify just as do the binary alloys from 1—4; furthermore, the alloys of the field 4—4—8—8, as those from 4—8; of the field 4—5—5—4, as those from 4—5, etc. (In this scheme it is to be noticed that the corresponding points have in all cases the same numbers.) To determine the composition of the solid phase separating from the liquid, it is necessary to pass a hori-

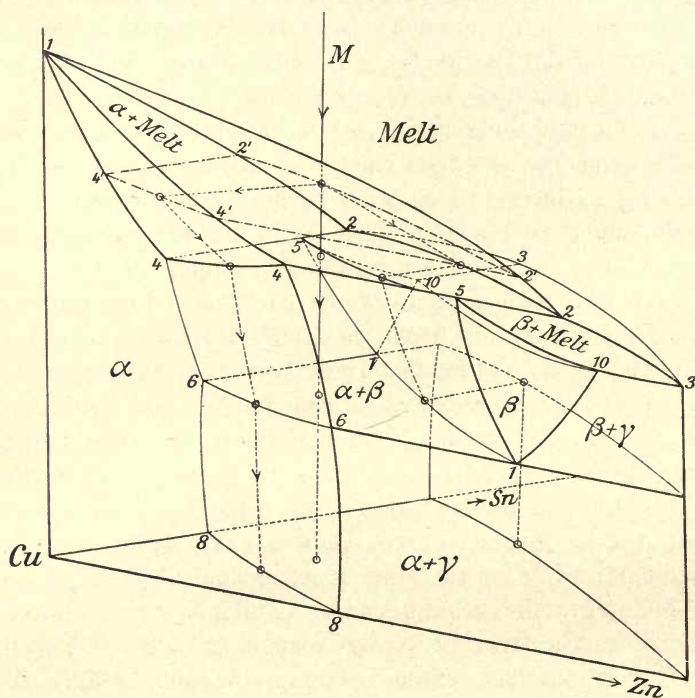


Fig. 2.

zontal plane (temperature) through the point in question on the liquidus surface, noting its intersection with the corresponding solidus surface. Now this temperature plane intersects the two surfaces in a line, so that we have two lines 2'—2' and 4'—4' running from the copper-tin system to the copper-zinc system, as shown for the two surfaces 1—4—4 and 1—2—2 in Figure 3. Along the lines 2—2' and 4—4', there will be pairs of concentrations in equilibrium with each other, as represented by the end points of the parallel lines. These lines, of course, are drawn in empirically and are intended to show

merely qualitatively the relation between the liquid and the solid in equilibrium.

For each temperature, such a plane, with coordinate points in the liquidus and solidus surfaces, could be constructed; and by means of such a diagram, the complete solidification of the alloy could be traced, and the composition of the phases at each temperature and the relative amounts of each phase corresponding, be determined. The relative amounts are to each other inversely as the distance of the phasial compositions from the characteristic line of the alloy, "characteristic line of the alloy" meaning the vertical corresponding to the total composition of the alloy. This method of determination may be applied in other fields of the diagram also. Thus far, in solidifying, the ternary alloys have behaved as simple solid solutions of tin + zinc in copper that is, as pseudo-binary alloys with copper as the solvent; moreover, except for what might at first seem to be irregularities due to the relative qualitative effect of the tin and the zinc, the kalchoids apparently undergo their transformations in the solid state analogously to the binary alloys. The field 4—8—8—4 gives the variation of saturated  $\alpha$  with temperature, the alloys in the field 1—8—8 at normal temperatures being simple homogeneous solid solutions. The surface 5—5—to 7—7, the conjugate surface to the surface 4—4—6—6, gives the variation of saturated  $\beta$  with temperature toward the copper corner. The line 7—7 connects the various eutectoid compositions from 26 per cent. tin to 48 per cent. zinc. The scheme discussed already may be used here in following the behavior of  $\alpha$  and  $\beta$  on cooling. The concentration of  $\alpha$  varies along the surface 4—4—8—8, while that of  $\beta$  varies along the surface 5—5—7—7. Disregarding for the moment complications in the pure copper-tin alloys, which doubtless extend some distance into the ternary diagram, on the  $\gamma$  side of the eutectoid line, the solid solutions  $\gamma$  and  $\beta$  are in equilibrium. The  $\beta$  solution follows the surface 10—10—7—7, the  $\gamma$  remaining fairly constant in composition on a nearly vertical plane through the " $\gamma$  line". Between these two regions, there is a region of pure  $\beta$  formed either by the peritectic reaction in the field 2—2—5—5 or from the liquid directly in the field 2—10—10—2. This field narrows down with a drop in temperature from the lines 5—5 and 10—10 to the eutectoid line 7. With this in mind, it is easy to see how the alloys in this region of pure  $\beta$  behave on cooling. In the solid bounded by surfaces 4—4—8—8 and a plane through the line 5—5, the alloys solidify as  $\alpha + \beta$ . In the little region bounded by the surface 4—4—8—8 and a vertical plane through 4—4, the  $\beta$

goes into solution on cooling. In the remainder of the solid,  $\alpha$  and  $\beta$  vary in composition on cooling, as given, until at the eutectoid point, the solution breaks up, giving the  $\alpha + \gamma$  complex. In the solid 5—5—7—7—10—10 corresponding to pure  $\beta$ , the alloys separate out primary  $\alpha$  on one side of the eutectoid line and primary  $\gamma$  on the other side. Along the line 7—7, of course, there is no primary segregation, the alloy going over into a simple eutectoid.

As regards the  $\beta$ -phase and its behavior in this series: in the pure copper-zinc system,  $\beta$  being one phase, and containing two components, has two degrees of freedom. At the breakdown  $\beta \rightleftharpoons \alpha + \gamma$  (there being now three phases), the system becomes non-variant, and so the change occurs with the temperature remaining constant. In the present case however, there are three components, the number of phases remaining the same; that is to say the system now has one degree of freedom at the moment of inversion. As the simplest case of this, we could have a breakdown corresponding to that found by Carpenter and Edwards in the copper-aluminium-zinc series, running from the one eutectoid point directly to the other, the temperature varying between the two end temperatures as a linear function of the concentration: in which case, one of the degrees of freedom is suppressed. Or the breakdown might just as well occur in a manner analogous to a series of solid solutions separating out of their melts, which series may run linear or have a maximum or a minimum. In this system a maximum is obtained near the middle point of the eutectoid line, as is seen from the section through the diagram along this line.

Another point of importance is the eutectoid structure. As is well known, the  $\beta$  constituent appears homogeneous under the microscope, but long annealing produces its true duplex structure. This is due to the fact that though the "apparent  $\beta$ " is composed of minute  $\alpha$  and  $\gamma$  particles, still these particles are so extremely fine, ultramicroscopic, that it is impossible to distinguish them. It is interesting to note what influence the addition of tin exerts: Do the  $\alpha$  and  $\gamma$  particles, their compositions thus changed, become enabled to coalesce into larger grains, thereby rendering themselves visible under the microscope? This problem has been discussed by Professor Carpenter<sup>1</sup>), who added tin in varying amounts to the pure apparent  $\beta$  constituent of the brasses, 48 per cent. zinc. This is shown diagrammatically in Fig. 3, in which the alloys having the desired tin content, are plotted by the points 1,

<sup>1</sup>) JInstMet 2 (1912) Vol. VIII.

2, 3, and 4. By drawing lines parallel to the eutectoid line, we obtain the approximate composition of the pure copper-zinc alloys having a corresponding microstructure. (The segregate shown in Professor Carpenter's microphotographs is therefore easily explained, and should not, on examination under a low power, be mistaken for a eutectoid structure. In a discussion of the microstructure for the purpose of studying the effect of tin addition on the apparent homogeneous structure of  $\beta$  constituent, it would be more proper to choose the compositions indicated by the points a, b, c, and d, which lie on the eutectoid line and contain the amounts of tin to be investigated. If in this manner a certain point can be located, beyond which the eutectoid structure is readily apparent, then it may be said that the percentage of tin added caused the visible breakdown of the  $\beta$  constituent. In reality this appearance does not confine itself to the eutectoid line, but may be followed over a field shown by the line 1—2, as may be clearly seen from an examination of the microstructure. But while the excess of the  $\gamma$  on the one side (or the excess of  $\alpha$  on the other) undoubtedly plays an important role in absorbing crystals of its own kind out of the ground mass, still the actual chemical composition and the rate of cooling seem to be the all-determining

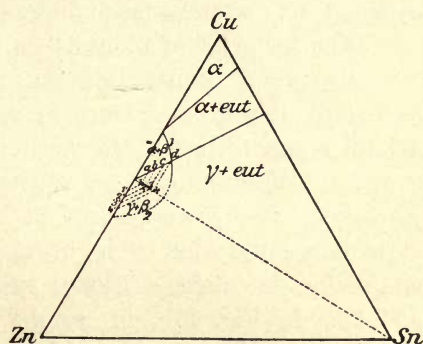


Fig. 3.

factors. In certain alloys (12) of the pure copper-zinc series (55 per cent.) and 45 of the ternary series, we have about the same relative proportions of segregate and ground-mass; but while the former alloys would probably require severe annealing just below the transformation point, the latter yields the eutectoid on normal cooling.

Professor Carpenter has called attention to an interesting point in connection with the  $\beta$  solution. He noticed the comparatively wide range in composition over which the alloys consisted of apparent  $\beta$ ; likewise, that immediately on entering the  $\beta + \gamma$  field, a much larger amount of  $\gamma$  was formed than would be expected from the position of the lines in the diagram. This led to the suggestion that the  $\beta$  solid solution was super-saturated, with respect to the  $\gamma$  solid solution, over the greater part of the homogeneous apparent  $\beta$  field. This range was considered by him to lie, therefore, on the Zn side of the true eutectic point.

Now to get an idea of the influence of time on the break-down, having considered that of the chemical composition, I compared chill-cast specimens, slowly cooled specimens, and annealed specimens. By plotting lines such as in Figure 3, to show the limiting compositions of the apparent  $\beta$  structure, it was seen that this field contracts toward the copper-zinc side as the time of cooling is increased. Two examples of this may be cited: alloy No. 6 (copper 57,4 per cent, tin 11,2 per cent, zinc 31,4 per cent) is shown as chill cast, Fig. 32a, and again, Fig. 32b, after being annealed 48 hours at 450 degrees C. In Fig. 32a, we have the  $\gamma$  segregate in a ground mass of apparent  $\beta$ , which, on examination of Fig. 32b, is seen to have been converted into  $\alpha$  plus  $\gamma$ . This conversion is evident from the increase in the relative amount of  $\alpha$ , and is also recognised on microscopical examination, when the solid solutions  $\alpha$  and  $\beta$  may usually be distinguished.

The behavior of alloy 54, which was cooled slowly in the furnace, was also very interesting. Superficially, this alloy consisted of the  $\gamma$  segregate in a ground mass of apparent  $\beta$ , but on examination under a higher magnification, it was found to be quite otherwise. Fig. 33a, shows the interior of a crystal and is seen to be, as above suggested,  $\gamma$  segregate plus apparent  $\beta$ . If we examine the edge of this crystal, we see that  $\beta$  is breaking down with the formation of the  $\alpha$  plus  $\gamma$  eutectoid. This may be seen on referring to Fig. 33b and 34. In Fig. 33b, in certain localities, there appears a parallelism in structure. This is the  $\alpha$  plus  $\gamma$  eutectoid, shown at better advantage in Fig. 34. This is seen very clearly under the microscope, but such a clear effect cannot be reproduced in photograph because of the haziness of the structure itself, and because of the nearly equal effect the colors of the various phases have on the photographic plate. Fig. 34 shows an area of well formed and unmistakable eutectoid structure, lamellar the same as on the  $\alpha$  side. From this it seems quite evident that considerable inertia must be overcome in order to bring about a visible resolution of  $\beta$ . The effect will be to lower the inversion temperature by supercooling, as well as to diffuse it over an interval of temperature, at times obliterating it altogether.

The fact that an appreciable amount of tin may be added to certain brasses without causing any noteworthy change of structure, is of decided practical importance. For a fuller appreciation of this fact, let us compare the structure of alloys in which tin is in apparent solution with that of those in which there is a visible breakdown. Take, for example, (1) an alloy in the group called by Thurston the "maximum

kalchoids" — that is, an alloy in the little field in which the tin goes into apparent solution (there the structure corresponds to that of the pure  $\beta$  constituent); (2) an alloy, for example No. 68 (see Figures 25 and 26), in which we have the eutectoid structure. That is to say, in the first alloy, the advantage of adding tin is fully realized, the alloy being able to retain the desirable structure; while in the second, the eutectoid structure is produced, the mechanical properties dropping in value to practically nil. The importance of locating the limits of this field is self-evident. Thurston has shown the rapid depreciation of the mechanical properties in this field upon the continued addition of tin to be much more rapid than is to be explained on the ground on the simple increase of tin content. Thus the tensile strength rises very rapidly from 50,000 to 65,000, then decreases sharply to 5,000 on crossing a relatively small area in composition.

The diagram shown in Fig. 4 and again on a larger scale in Fig. 5 was constructed on thermal and micrographical evidence, using the scheme suggested by the perspective in Fig. 2 as a guide. Little need be said concerning the determination of the liquidus and solidus surfaces. The two binary diagrams of Shepherd were used as a basis for constructing the liquidus surface, the corresponding temperatures being projected on to the ternary diagram. Then the direction of each contour was determined by plotting the melting points obtained in the research. These melting points may be seen on reference to the curves given in connection with this paper. These alloys are subjected to very little super-cooling and the temperature marking the beginning of a change in the cooling curve was accepted as being the melting point. As is common to this method of thermal analysis, points on the solidus surfaces were obtained much less satisfactorily. Allowing for experimental error, these lines run uniformly through the field. The changes in direction which the contours take on crossing 2—2, though not pronounced, can always be clearly seen; and this method of locating line 2—2 checked nicely with the other more accurate method (i. e. that of locating the line by using the peritectic transformation point) which was employed.

The peritectic is to be seen very clearly on the cooling curves. This heat effect varies in intensity in the ternary diagram as it does in the two binary systems. It is much more pronounced in the tin-rich kalchoids and less so in the zinc-rich kalchoids. The line 2—2 is therefore determined by the concentration at which this heat effect drops out. On crossing the line 2—2 on the tin side of the diagram, a

second peritectic reaction is noted on the cooling curves. On the Zn side, this heat effect was not noticed, in which case the alloys solidified as simple solid solutions. Miller's determinations were plotted but found to be too irregular for use here. The solidus surfaces, as determined from the cooling curves, are seen to run underneath the liquidus surfaces as indicated in Fig. 2. The surface 1—4—4 was not determined. The surface 4—4—2—2 was found to run irregularly from the one binary series to the other, upon the addition of tin, dropping rather rapidly from the copper-zinc side until it ran nearly horizontal to the copper-tin side. Between the lines 5—5 and 2—2, the surface drops until it reaches line 2—2. From line 2—2 to line 10—10, the

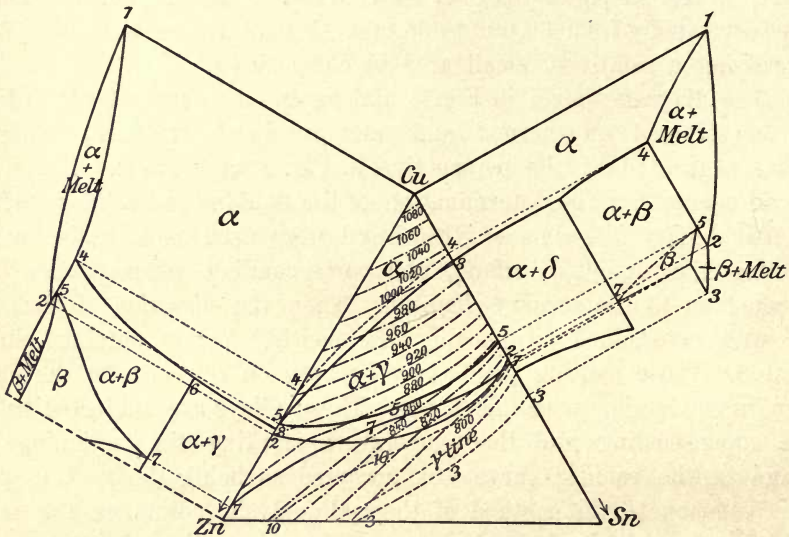


Fig. 4.

alloys solidify over a small interval of temperature, giving the  $\beta$  solid solutions. The line 10—10 was located by observing at what compositions the second peritectic reaction ( $\beta$  plus liquid =  $\gamma$ ) entered. Several of the cooling curves taken in this field are included to show the type of cooling curves obtained and the appearance of the peritectic heat effect. With these curves, the lines 5—5 and 2—2 may be followed throughout the diagram. The actual location of line 5—5 is simplified considerably by noting the return of the cooling curve from the peritectic reaction. If the return is gradual, the alloy is still part liquid and solidifies further, according to the reaction  $\beta + \text{melt} \rightleftharpoons \beta$ . If the return is sharp, the alloy goes solid with the peritectic reaction.



Transformations in the solid state may be followed in a similar manner to that just discussed.

Considering first a section through the diagram along the eutectoid line 7—7, we see, as stated above, that instead of running linear from copper-zinc to copper-tin it rises to a maximum near the middle, corresponding to 590 degrees C. (using the mean of the temperatures on heating and cooling). This inversion point, as obtained from the cooling curve taken direct from the liquid, is subject to super-cooling.

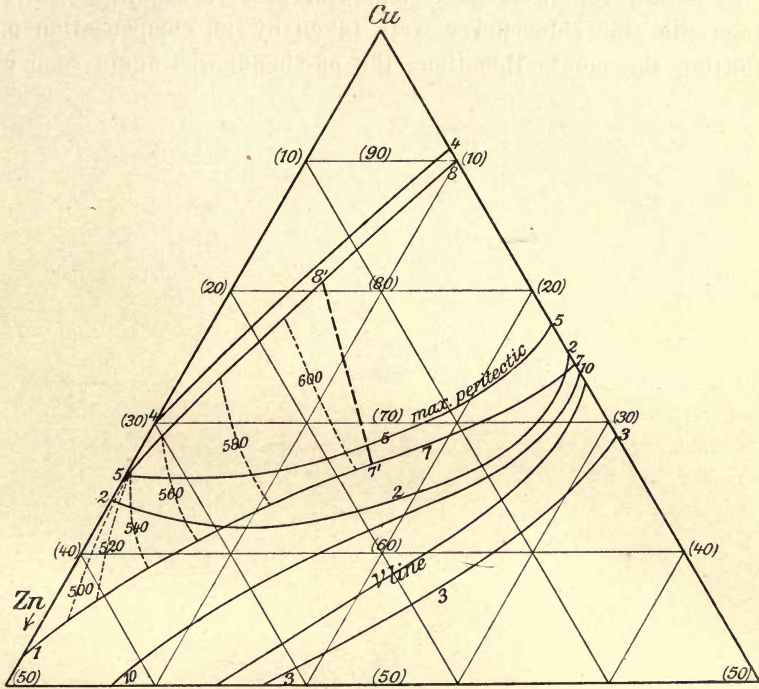


Fig. 5.

The most noticeable effect of super-cooling occurs in the alloys with small per cent tin just off the copper-zinc diagram; here the inversion point is either so weak or so diffused as to be scarcely recognisable. That this should be so is a natural conclusion from the discussion of the influence of tin on the inversion. Beyond 10 per cent tin the point is clear and well defined, but still subject to a super-cooling of from 15 degrees to 30 degrees — taking the maximum difference between the point on heating and the (same) point on cooling. When the maximum is passed, the inversion drops off regularly toward the

copper-zinc series. These points may be followed by reference to the cooling curves taken direct from the melt which were mentioned above. The irregularities in the cooling curves for alloys in the region of apparent  $\beta$  may be seen by reference to curves 55—56—58—59—63—64. With the addition of 10 per cent tin or more, the eutectoid point is seen much more clearly, as on curves 50—51 and 53. In the field of the  $\alpha + \beta$  bronzes, the curves exhibit two heat effects, which may be seen on curves 72—73—74—75 and 76.

To obtain the inversion temperatures more accurately, and especially on the zinc side curves were taken by the compensation method. On plotting the points this time, the maximum was again seen clearly,

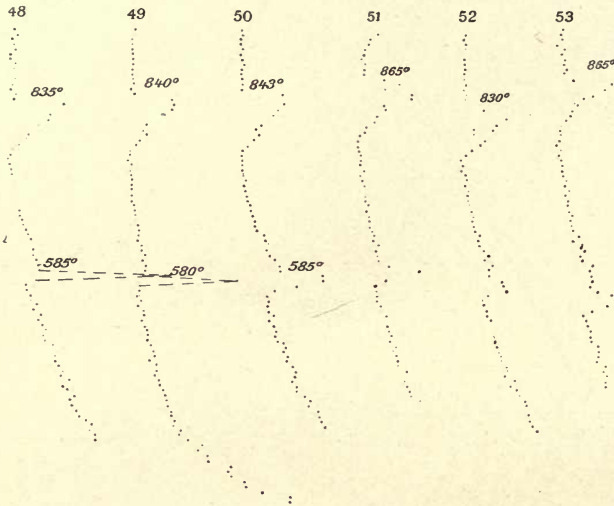


Fig. 6.

and a rise in the individual temperatures was observed. See curves 42, 58, 53 and 51. It was interesting to note how the addition of only one per cent tin was sufficient to raise the inversion temperature of  $\beta$  brass from 477 degrees to 495 degrees C., a good example of the enormous influence which the addition of even quite small proportions of a third element may exert.

Another point under consideration was whether the heat-effect took place at a constant temperature or over an interval of temperature, forming in this way a major and a minor curve intersecting at the maximum. The determination of this point — a thing possible enough theoretically — is made considerably more difficult by the fact that the

heat-effect is diffused over an interval, through the inherent nature of the reaction. It can be said with certainty that the inversion does occur at constant temperature at the maximum, and that on either side it has the appearance of being an interval.

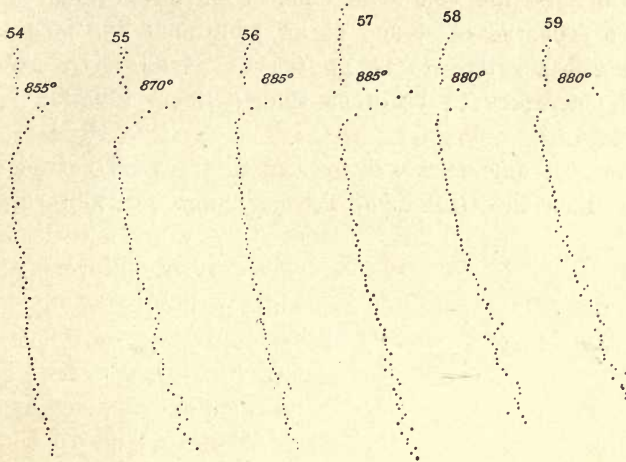


Fig. 7.

The temperature of the eutectoid point is raised with increase in the copper content also, so that the effect on the inversion temperature

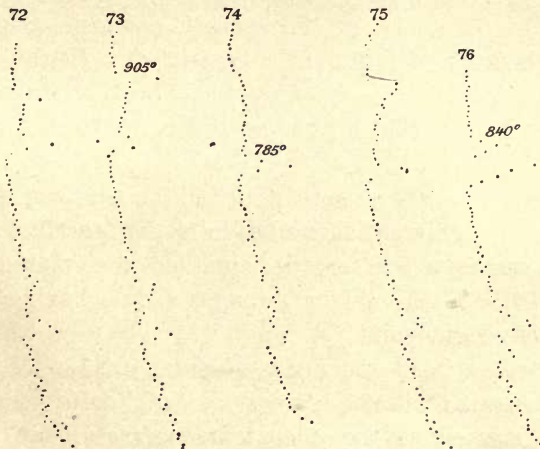


Fig. 8.

of the brasses produced by the addition of tin, is in turn remarkably increased with the increase in copper. See curve 60. On crossing the

line 2—2 when above the eutectoid section 7—7, this rise in temperature is very rapid — which fact leads to speculation as to why this happens. The 3 tin, 29 zinc alloy, for example, shows an inversion temperature of 570 degrees C. as compared to 480 degrees in an alloy of 6 tin and 33.5 zinc, which is just below the line. From this evidence, one might be led to suspect the existence of an additional line in the diagram; but outside of this there was no reason at all for considering the change in temperature to be other than a linear function of the composition.

The greatest deviation was noticed in the field between the lines 7—7 and 8—8 on the tin side of the maximum. Much to my astonishment two well defined heat-effects were recorded on every alloy tested in this region both on the first or direct curve and on the compensation curve. For example, see Fig. 9, which is the heating curve of an alloy with 15 per cent tin and 10 per cent zinc with its first derivative.

The curves taken of the alloys in this region pointed to the possibility of a transformation point in the pure copper-tin alloys at about 600 degrees C., which seems the most

satisfactory explanation of this double heat-effect. In the binary alloys, this upper heat effect might be very weak (an ordinary cooling curve failing to show it, see Fig. 1), but with the addition of zinc might be appreciably strengthened.

Accordingly, five alloys were made up for the purpose of studying this point, and the differential method already described was used for recording the curves. The curves obtained are plotted in Fig. 10. These alloys all lie in the  $\alpha$  plus  $\beta$  range, alloy e having a composition very near the eutectoid point.

As expected, a heat-effect was recorded at 590 degrees C., very weak compared to that at 525 degrees, but still quite perceptible. This effect is more marked as the  $\beta$  content increases, but when the tin content is as much as 25 per cent it has disappeared entirely. This heat-effect can be explained on the assumption of a new line in the diagram, this new line corresponding to an inversion  $\beta \rightleftharpoons \alpha + \gamma$ . The second heat-effect at 525 degrees would in this case correspond to the

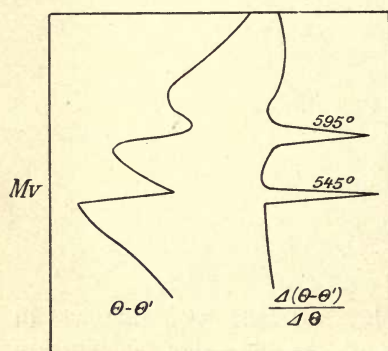


Fig. 9.

inversion  $\gamma \rightleftharpoons \alpha + \delta$ . The increase in the upper heat-effect as the  $\beta$  range is passed through and its disappearance as the eutectoid composition is reached would support this view. However, it will be seen later under a discussion of the micro-structure that this explanation is in reality untenable. The explanation of the heat-effect at 590 deg. is impossible at this time, as it will be necessary to perform considerable more experimental work. It has been suggested to me by Professor Carpenter that the double heat-effect might be due to a super-cooling of the  $\beta$  constituent, the lower heat-effect representing the limit of super-cooling. The proper temperature of the inversion would be 590 deg. This explanation would serve to reconcile the discrepancies in the above mentioned literature as to the temperature of the eutectoid inversion. This temperature has been given from 480 deg. to 525 deg., or, over a range of 45 deg., a limit of error much greater than the experimental

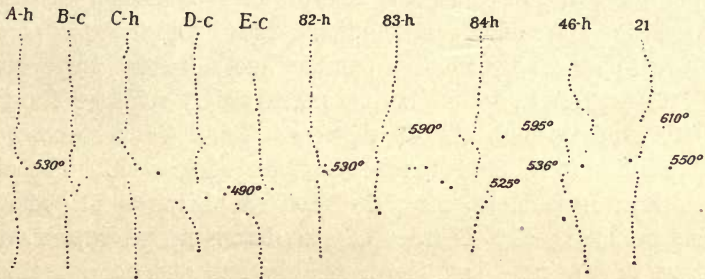


Fig. 10.

error. The addition of zinc influences these points in two ways: (1) the temperature undergoes a small rise accompanied by (2) a strong increase in the upper heat-effect as compared to the lower. This rise in temperature, appreciably noticeable only after the addition of considerable zinc, is about 15 degrees over the entire range. The upper heat-effect is already strong with 3 per cent zinc addition, as seen from curves 82, 83 and 84 Fig. 10. Further addition of zinc causes a remarkable increase, as is seen from curves 46 and 21 Fig. 10. Thus the upper heat-effect becomes even stronger than the lower one till the latter, on reaching the line 7'—8', disappears entirely.

The ternary system being considered as pseudo-binary, one degree of freedom is suppressed, and the transformations take place in the same manner as in the pure copper-tin alloys; hence a copper-rich solid solution will always be in equilibrium with a copper-poor solid solution. Such an assumption requires that the relative amounts of tin and zinc

remain the same in the phases present. The temperatures at which the transformations occur may of course vary and, as is actually the case, a maximum is obtained near the middle, at the line 7'—8'. This is to be expected; for as the compositions of these phases vary, it is natural to have different temperatures at which saturation (separation of segregate) and mutual saturation (formation of eutectoid) occur.

At the line 7'—8' the heat-effect at 525 degrees C. disappears, probably because the two phases  $\beta$  and  $\beta'$  become mutually soluble at this line.

A micrographical study was likewise made of the alloys exhibiting the double heat-effect. Three specimens of the alloy D were heated in a small electric furnace to 675 degrees C., and annealed for thirty minutes. Then, by gradually increasing the resistance, the temperature was lowered, and at 610 degrees C. (thirty minutes being required for the temperature to fall thus far) one of the specimens was quenched. Again increasing the resistance, the temperature was lowered very slowly through the upper transformation point, when a second piece was quenched at 565 degrees C. — it having taken thirty minutes for the temperature to drop through the 45 degrees. Then the current was switched off, and the third piece quenched at 430 degrees C. The structure of these three specimens may be seen in Figures 11, 12 and 13. The structure above 610 degrees C. is shown to be duplex, while at 430 degrees C. we have just the normal bronze structure in this range. What is quite surprising is that, on passing the first heat-effect (see Fig. 12), a third phase formed as a broad band around the  $\alpha$  crystals. From this peculiar occurrence we might conclude that the upper heat-effect is due to the formation of the band, and that the second heat-effect is due to the breakdown of the remaining  $\beta$  crystals between the bands. On repeating the experiment, but annealing this time for three hours at 565 degrees C. before quenching, a greater break-down of the  $\beta$  constituent was produced, the gray band having grown broader and large gray islands having formed throughout the  $\beta$ . (See Fig. 14.)

The above evidence does not support the assumption of two heat-effects corresponding to  $\beta \rightleftharpoons \alpha + \gamma$  and  $\gamma \rightleftharpoons \alpha + \delta$ . Indeed it seems rather to indicate a very tardy formation of a single eutectoid. This latter is readily acceptable, on the assumption that the lower heat-effect is due to super-cooling of the  $\beta$  phase. The formation of the eutectoid would then proceed at a rate which depended upon the temperature. This rate would reach a maximum at a temperature below the actual inversion temperature and on these grounds one might expect an appreciable

change in the rate of formation of the eutectoid, depending directly on the annealing temperature. That this is actually the case may be seen by reference to Figs. 12, 13 and 14. The formation of the eutectoid evidently proceeded very slowly with the specimen which was annealed

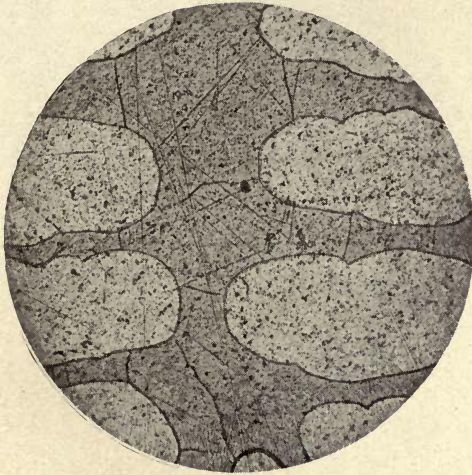


Fig. 11. Alloy D.  
Cu 78.0 Quenched from 650° C.  
Sn 22.0  $\alpha + \beta$ .



Fig. 12. Alloy D.  
Cu 78.0 Quenched from 565° C.  
Sn 22.0 Three phases.

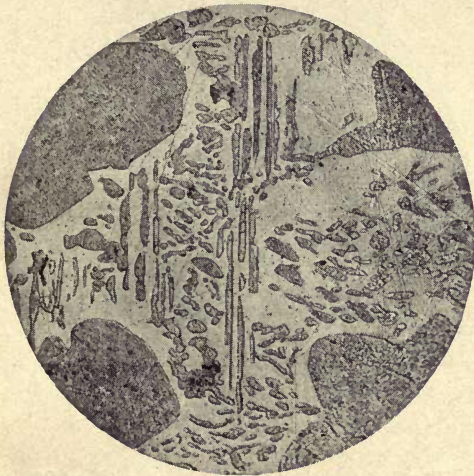


Fig. 13. Alloy D.  
Cu 78.0 Quenched from 430° C.  
Sn 22.0  $\alpha + \text{eutectoid}$ .



Fig. 14. Alloy D.  
Cu 78.0 Annealed at 565° C.  
Sn 22.0 For 3 hours and quenched.

at 565 deg. If annealed at a temperature under 500 deg., such as is the case in Fig. 13, the eutectoid formed much faster and the normal eutectoid structure was formed. If  $\beta$  solid solution is in reality sub-

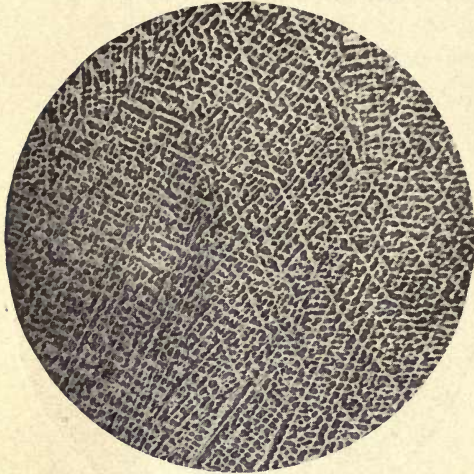


Fig. 15.  $\times 100$  Alloy 7.  
Cu 88.5  
Sn 7.9  
Zn 3.6.  
Annealed at 450° C.  
 $\alpha$ .

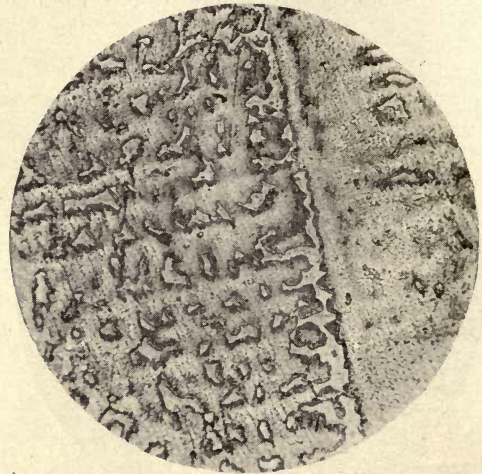


Fig. 16.  $\times 450$  Alloy 21.  
Cu 78.6  
Sn 9.8  
Zn 11.6.  
chill cast.  
 $\alpha + \gamma$ .



Fig. 17.  $\times 450$  Alloy 23.  
Cu 77.2  
Sn 5.6  
Zn 22.2.  
Annealed at 450° C.  
 $\alpha + \gamma$ .



Fig. 18.  $\times 450$  Alloy 20.  
Cu 66.2  
Sn 4.2  
Zn 29.6.  
Annealed at 450° C.  
 $\alpha + \gamma$ .



jected to super-cooling, then a heating curve should show no heat-effect at 525 deg. C. This is not true to fact, for each alloy in this range exhibits heat-effects at both 525 deg., and 590 degrees, both on heating and cooling.

So far, I have found no one diagram to explain these facts altogether satisfactorily; nevertheless, the necessity of reconstructing the copper-tin diagram seems very certain. But to do this, longer annealing is required. For example, it will be necessary to anneal at a temperature intermediate between the two heat-effects until stable equilibrium is reached, and then on cooling note the influence on the lower heat-effect.



Fig. 19.  $\times 150$  Alloy 12.  
Cu 78.2 chill cast.  
Sn 15.5  $\alpha + \gamma$ .  
Zn 6.3.

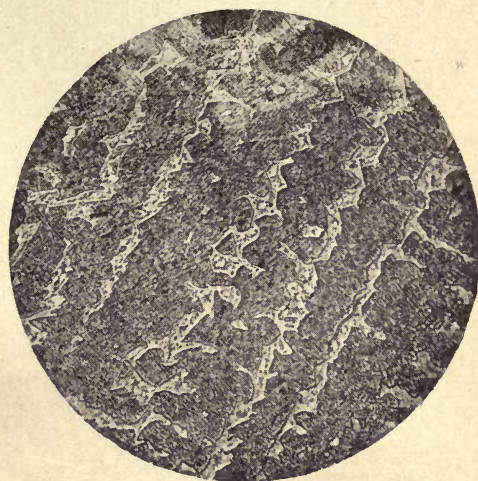


Fig. 20.  $\times 560$  Alloy 12.  
Cu 78.2 chill cast.  
Sn 15.5  $\alpha + \gamma$ .  
Zn 6.3.

**Microstructure.** The microstructure of the ternary alloys corresponds very closely to that of the two binary systems; hence it will not be necessary to present microphotographs covering the entire field. In the field 1—8—8, we have simple solid solutions; as shown, for example, in Fig. 15, which exhibits the dendritic structure so characteristic of the alloys in this field. At this magnification, the structure has a duplex appearance; but on examination under a higher power, this appearance is clearly shown to be due to the inhomogeneity of the dendritic structure. On crossing 8—8, small islands of a gray constituent arranged according to the prevailing dendritic structure can be seen. This is

the  $\gamma$  solid solution. Figs. 16, 17 and 18, show alloys which have an appreciable amount of the  $\gamma$  phase present. These alloys lie about

the same distance off 8—8. From these microphotographs the difference in structure of cast and annealed specimens is plain to be seen; the eutectoid disappears with annealing. Fig. 19, gives the general structure of these alloys; Figs. 20 and 21, the eutectoid. As we go further into the diagram, the eutectoid is found to increase quite rapidly, as seen from Figs. 22, 23 and 24. Little change in the microstructure occurs in sections running parallel to 7—7 until the copper-zinc side is neared. Here the structure of the alloys with a zinc content lower than 35 per



Fig. 21.  $\times 2050$   
Cu 78.2  
Sn 15.5  
Zn 6.3.

Alloy 12.  
chill cast.  
 $\alpha + \gamma$ .

cent. is the same as that of alloys with a higher tin content; and the complications due to the  $\beta$  break-down are not met with. But on increasing the zinc content, we go over from the stable to the unstable structures (shown by the line 1—2 in Fig. 3), passing through a zone whose alloys usually show three constituents present. When we reach the unstable field, the structures of the brasses are prevalent



Fig. 22.  
Cu 69.0  
Sn 10.0  
Zn 21.0.

$\times 360$ . Alloy 70.  
Slowly cooled in furnace.  
Primary  $\alpha +$  eutectoid.

$\alpha$  needles in a ground mass of apparent  $\beta$ . By noting the change in microstructure from primary  $\alpha$  dendrites to  $\alpha$  segregate, we can check the location of line 5—5.

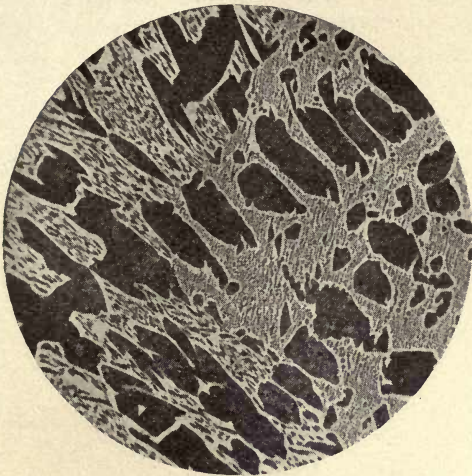


Fig. 23.  $\times 150$  Alloy 71.  
Cu 70.0 Slowly cooled in  
Sn 14.0 furnace.  
Zn 16.0 Primary  $\alpha + \text{eutectoid}$ .

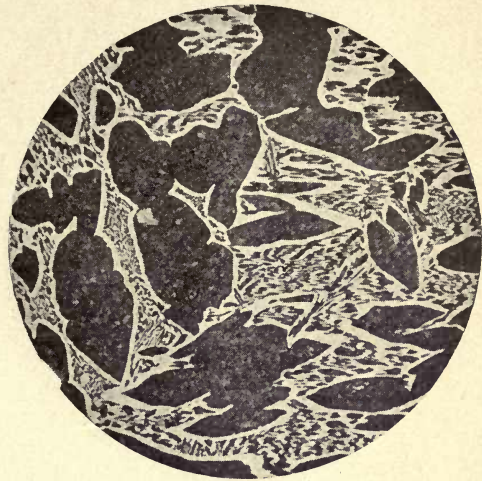


Fig. 24.  $\times 180$  Alloy 69.  
Cu 67.0 Slowly cooled in  
Sn 8.0 furnace.  
Zn 25.0 Primary  $\alpha + \text{eutectoid}$ .



Fig. 25.  $\times 10$  Alloy 68.  
Cu 60.4 Slowly cooled in  
Sn 6.0 furnace.  
Zn 33.6  $\alpha + \gamma$  eutectoid.

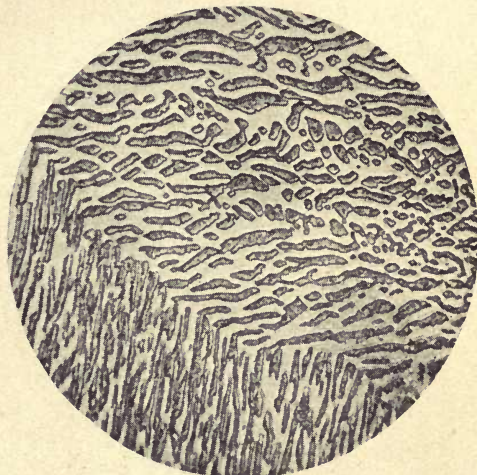


Fig. 26.  $\times 1250$  Alloy 68.  
Cu 60.4 Slowly cooled in  
Sn 6.0 furnace.  
Zn 33.6  $\alpha + \gamma$  eutectoid.

In Figs. 25 and 26, the pure eutectoid structure is exhibited. From Fig. 25, we see how uniformly the inversion takes place throughout, and how the eutectoid forms colonies, much the same as the eutectic

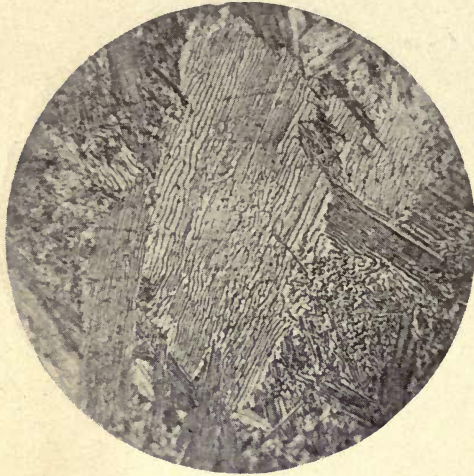


Fig. 27.  $\times 1040$  Alloy 31.  
Cu 61.0 chill cast.  
Sn 8.0  $\alpha + \gamma$  eutectoid.  
Zn 31.0.

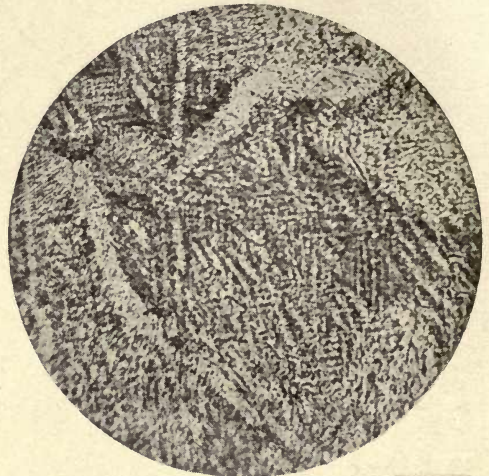


Fig. 28.  $\times 1250$  Alloy 34.  
Cu 70.0 chill cast.  
Sn 20.0  $\alpha + \gamma$  eutectoid.  
Zn 10.0.

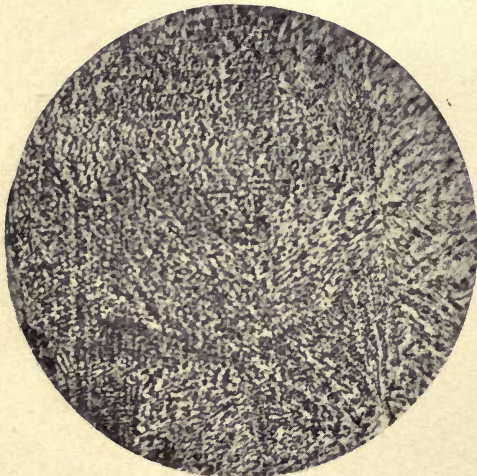


Fig. 29.  $\times 1250$  Alloy 34.  
Cu 70.0 chill cast.  
Sn 20.0  $\alpha + \gamma$  eutectoid.  
Zn 10.0.

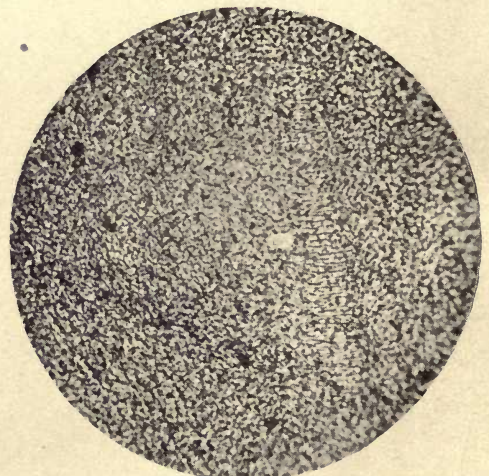


Fig. 30.  $\times 1250$  Alloy B1.  
Cu 95.0 Slowly cooled in  
Sn 0.0 furnace.  
Zn 5.0  $\alpha$ .

Ledeburite described by Professor Benedicks; further its similarity to Pearlite is evident from Fig. 27. The structure of the eutectoid with small percentages of tin is that of free  $\beta$  of the brasses and likewise

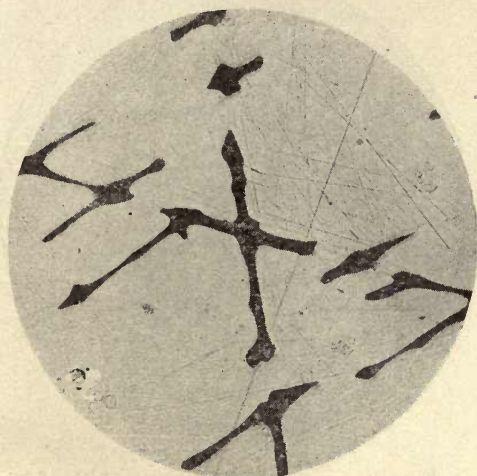


Fig. 31.  $\times 135$  Alloy 79.  
 Cu 50.0  
 Sn 10.0  
 Zn 40.0  
 Slowly cooled in furnace.  
 $\gamma + \text{app. } \beta$ .

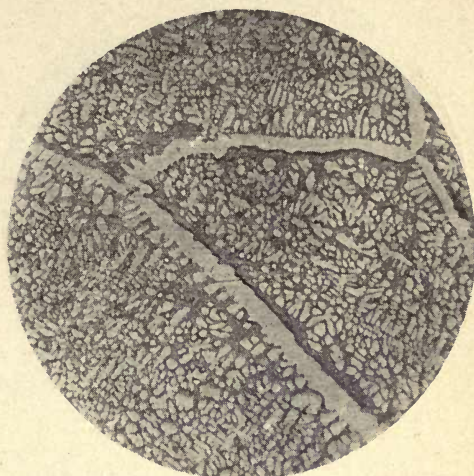


Fig. 32a.  $\times 450$  Alloy 6.  
 Cu 57.4  
 Sn 11.2  
 Zn 31.4  
 chill cast.  
 $\gamma + \text{app. } \beta$ .

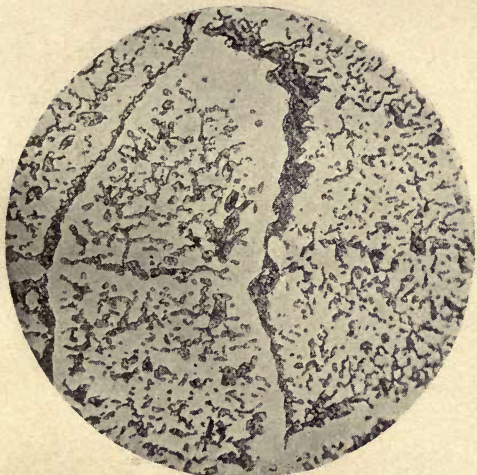


Fig. 32b.  $\times 450$  Alloy 6.  
 Cu 57.4  
 Sn 11.2  
 Zn 31.4  
 Annealed at 450° C.  
 $\gamma + \alpha$ .



Fig. 33a.  $\times 700$  Alloy 54.  
 Cu 58.0  
 Sn 8.0  
 Zn 34.0  
 Slowly cooled in furnace.  
 $\gamma$ -Segregate + app.  $\beta$ .

is also not confined to a line but extends over a small percentage perpendicular to line 7—7.

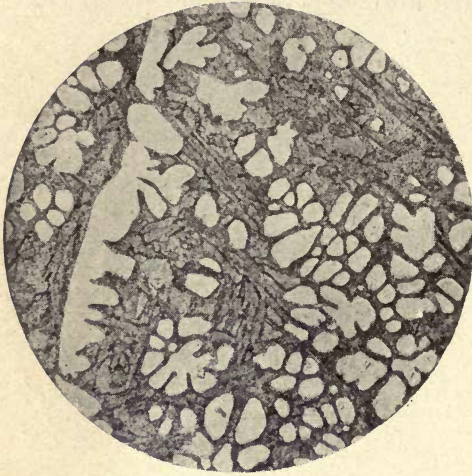


Fig. 33b.  $\times 450$  Alloy 54.  
Cu 58.0 Slowly cooled in  
Sn 8.0 furnace.  
Zn 34.0.

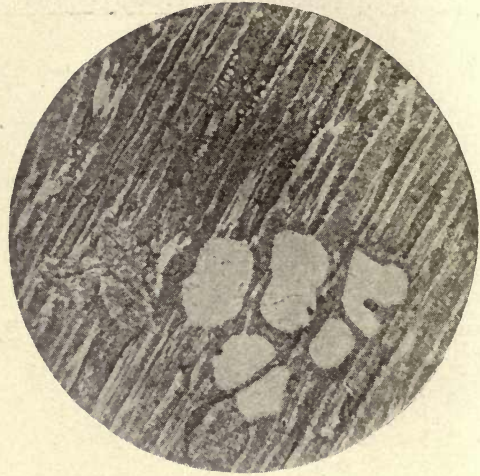


Fig. 34.  $\times 1000$  Alloy 54.  
Cu 58.0 Slowly cooled in  
Sn 8.0 furnace.  
Zn 34.0.  $\beta = \alpha + \gamma$  Inversion.



Fig. 35a.  $\times 40$  Alloy 48.  
Cu 66.0 Slowly cooled in  
Sn 17.0 furnace.  
Zn 17.0.  $\gamma +$  eutectoid.



Fig. 35b.  $\times 210$  Alloy 48.  
Cu 66.0 Slowly cooled in  
Sn 17.0 furnace.  
Zn 17.0.  $\gamma$  segregate + eutectoid.

Working with the microstructure of the eutectoid and apparent  $\beta$ , seeking to get reproductions of them which would show the duplex

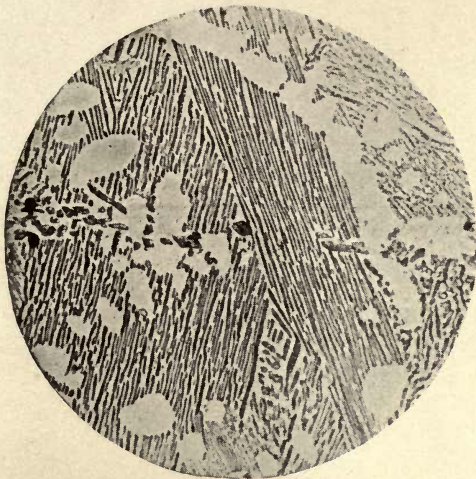


Fig. 36.  $\times 750$  Alloy 48.  
 Cu 66.0 Slowly cooled in  
 Sn 17.0 furnace.  
 Zn 17.0  $\gamma$  segregate + eutectoid.



Fig. 37a.  $\times 40$  Alloy 78.  
 Cu 65.0 Slowly cooled in  
 Sn 25.0 furnace.  
 Zn 10.0  $\gamma$  + eutectoid.

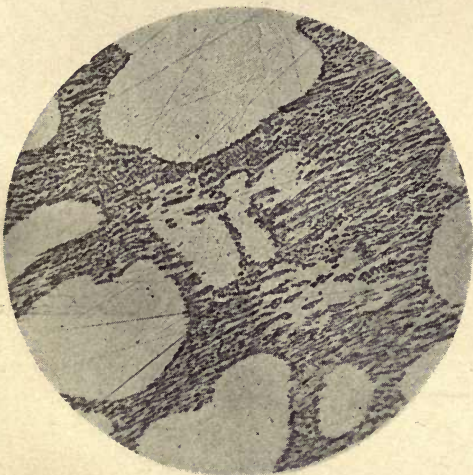


Fig. 37b.  $\times 700$  Alloy 78.  
 Cu 65.0 Slowly cooled in  
 Sn 25.0 furnace.  
 Zn 10.0  $\gamma$  + eutectoid.

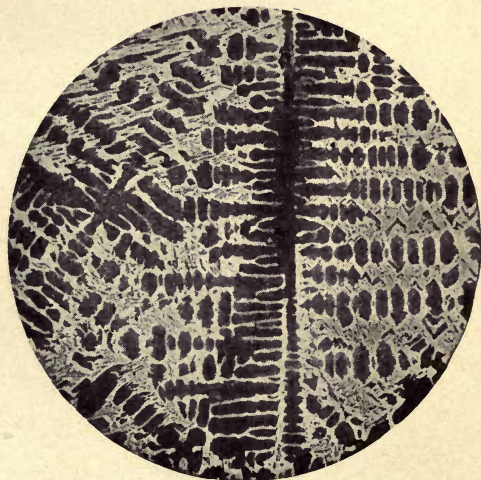


Fig. 38.  $\times 35$  Alloy 73.  
 Cu 75.0 Cooled slowly in furnace.  
 Sn 15.0  $\alpha$  +  $\gamma$  (in three  
 Zn 10.0 generations).

structure, I was struck with the great difficulty in actually showing that a structure is in reality heterogeneous. Interesting in this con-

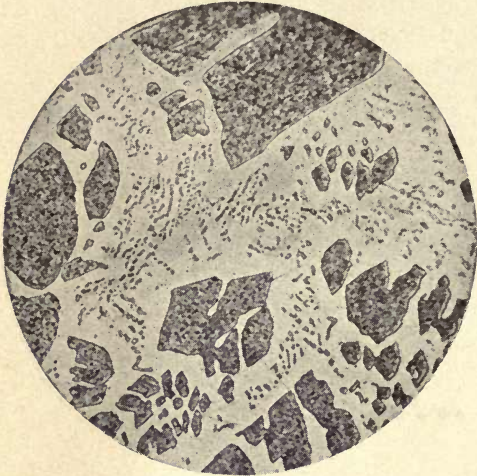


Fig. 39.  $\times 1250$  Alloy 73.  
Cu 75.0 Cooled slowly in furnace.  
Sn 15.0  $\alpha + \gamma$  (in three  
Zn 10.0 generations).

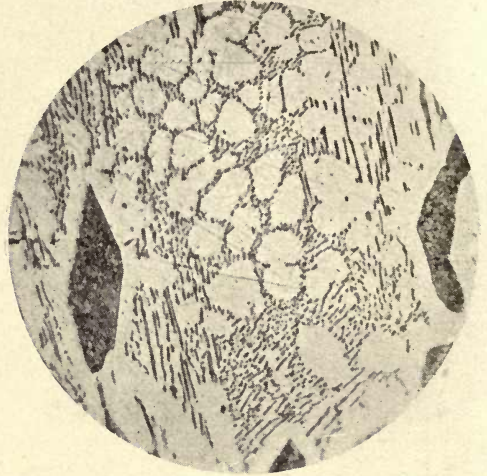


Fig. 40.  $\times 1250$  Alloy 73.  
Cu 75.0 Annealed at 700° C. and  
Sn 15.0 slowly cooled in furnace.  
Zn 10.0.  
 $\alpha$  (2nd and 3rd generations) +  $\gamma$ .

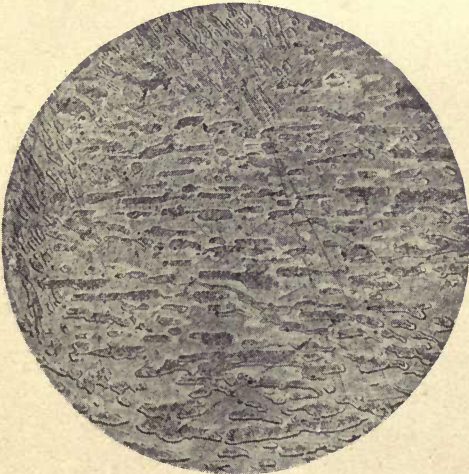


Fig. 41.  $\times 500$  Alloy 46.  
Cu 69.5 Annealed at 560° C.  
Sn 20.0 and quenched.  
Zn 10.5.

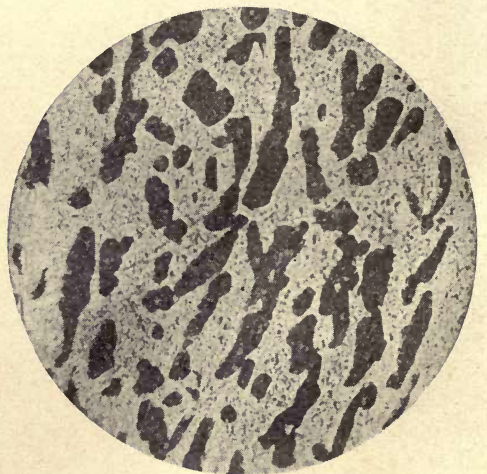


Fig. 42.  $\times 1000$  Alloy 46.  
Cu 69.5 Quenched from 560° C.  
Sn 20.0 and annealed at 450° C.  
Zn 10.5.



nection are Fig. 28, and Figs. 29 and 30, which represent extreme cases showing a structure known to be heterogeneous alongside of one considered to be homogeneous.

Fig. 28 shows an alloy of eutectoid composition which has been chill cast, giving an extremely fine structure, and the different tones produced can easily lead to the deduction that two constituents are present, a light and a dark one; in Fig. 29 a field is represented which overlaps the field of Fig. 28, Fig. 29 showing a coarser structure of the same specimen. A third picture (of a five per cent. brass), taken under identical conditions, is Fig. 30. Since a comparison of a structure known



Fig. 43.            × 135            Alloy 73.  
Cu 75·0            Annealed at 560° C.  
Sn 15·0            quenched.  
Zn 10·0.

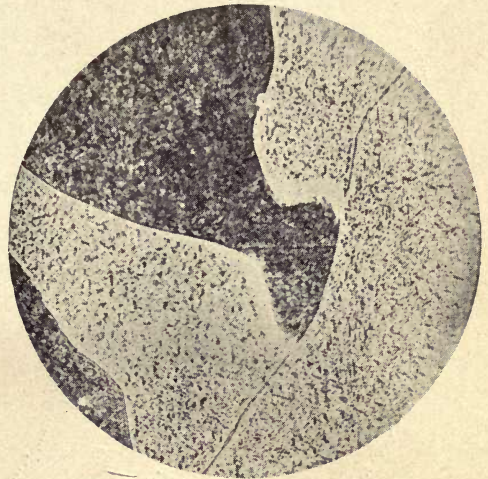


Fig. 44.            × 1250            Alloy 73.  
Cu 75·0            Annealed at 560° C.  
Sn 15·0            quenched. Annealed  
Zn 10·0.            at 450° C.     $\alpha + \gamma$ .

to be heterogeneous with that of a homogeneous structure fails to bring out the difference one might expect, it is clear that a microphotograph can not be taken as final or conclusive evidence that a doubtful structure is either heterogeneous or homogeneous.

On the  $\gamma$  side we may have either  $\gamma$  plus apparent  $\beta$  in the zinc-rich alloys or  $\gamma$  plus the eutectoid.  $\gamma$  plus apparent  $\beta$  (with varying amounts of  $\gamma$ ) is to be seen from Figs. 31, 32 and 33. The eutectoid structure is given in Figs. 34, 35, 36 and 37b.

Taking up now the microstructure of the alloys in the field exhibiting the two heat-evolutions: in Fig. 38, we have an alloy

of 15 per cent. tin and 10 per cent. zinc which was cooled slowly in the furnace. Three generations of  $\alpha$  are evident: (1) the  $\alpha$  dendrites, (2) the small  $\alpha$  crystals between them forming an apparent eutectoid structure, and (3) the very minute  $\alpha$  crystals in the part which appears gray. These are to be seen more clearly in Fig. 39. By annealing a specimen for three hours above the transformation points and allowing it to cool slowly in the furnace, the characteristic structure of this alloy was obtained, as shown in Fig. 40, where the peculiar crystallization in the  $\gamma$  phase is conspicuously evident.

Micrographical experiments upon an alloy lying on the line 7—7 of Fig. 4 showed that this line must be moved, to correspond approxi-

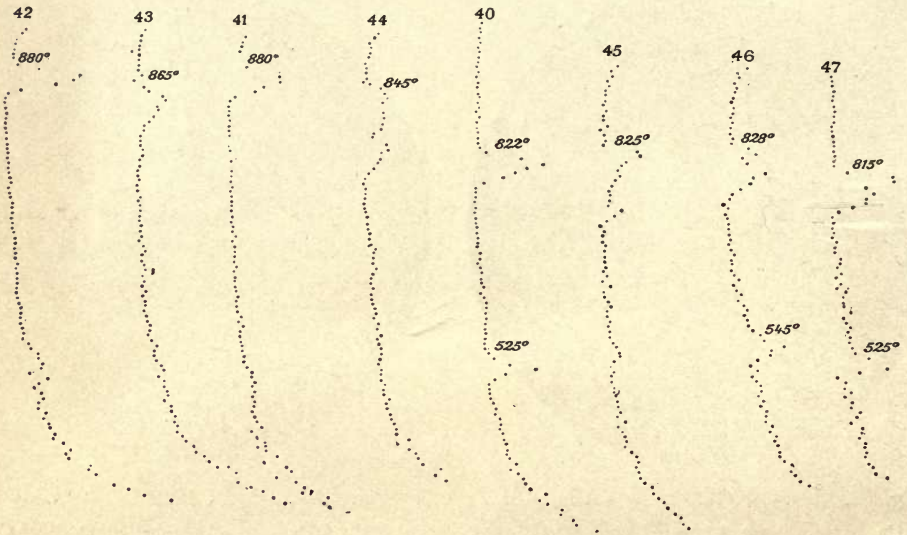


Fig. 45.

mately to the position as shown. The normal structure of this alloy on cooling is the same as that shown in Fig. 29, which is a very fine-grained eutectoid; hence its normal structure places it at once on the eutectoid line. However, annealing at 565 degrees C. and quenching, gives a heterogeneous and eutectoid-like structure, as represented by Fig. 41. This would correspond to the  $\alpha$  plus  $\beta$  structure of the new diagram. On annealing again for forty-five minutes by gradually raising the temperature to 460 degrees C. and again cooling, the  $\beta$  constituent breaks down, giving the structure shown in Fig. 42.

Alloy 73 behaves on thermal treatment similarly to alloy D, except that under certain conditions three generations of  $\alpha$  may form see

Figures 38 and 39. Annealing at 560 degrees C. for thirty minutes and quenching gives the structure shown in Fig. 43 —  $\alpha$  dendrites with

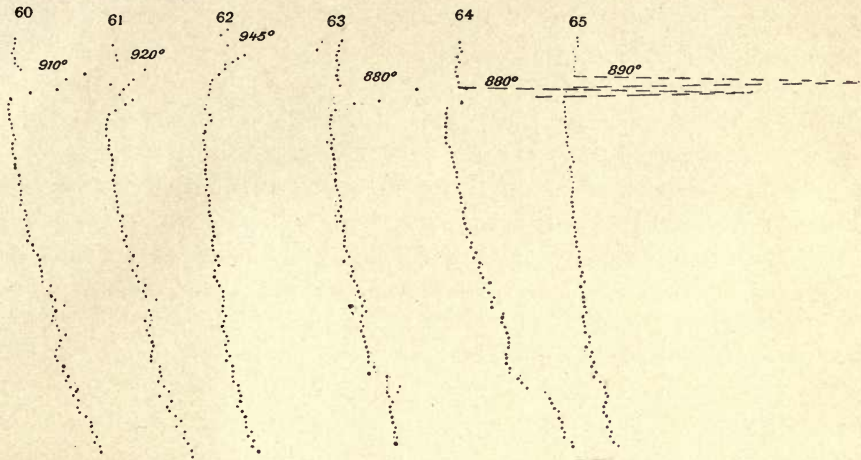


Fig. 46.

the  $\beta$  solid solution in between. The thin gray border cannot be seen at this magnification. Annealing the specimen a short time at 450 degrees C. gives the break-down as shown in Fig. 44. Annealing for

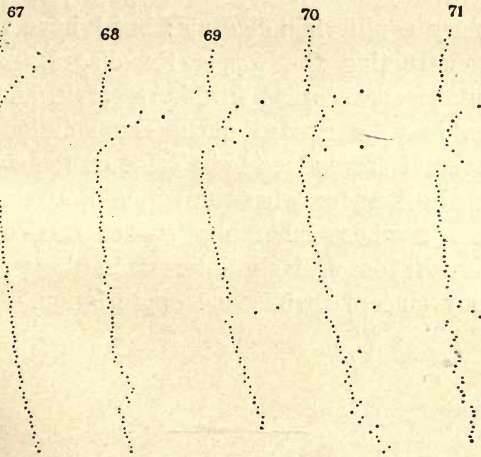


Fig. 47.

thirty minutes at 700 degrees C., cooling slowly to 560 degrees C., and quenching, gives a different structure (from that of Fig. 43), in that small  $\alpha$  crystals have formed in between the larger dendrites, evidently the second generation earlier referred to. The structure in Fig. 39,

offers no proof as to whether the second and third generations of  $\alpha$  are the same phase, but in as much as the  $\beta$  phase on annealing below

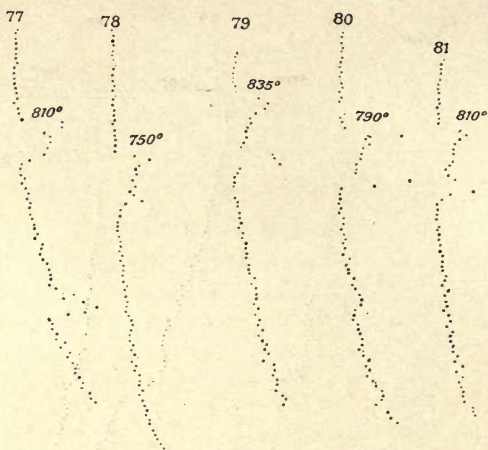


Fig. 48.

545 degrees C. gives a very regular duplex structure (Fig. 44), there can be no doubt that they are the same phase — a fact which must be true if these alloys are pseudo-binary.

I have not attempted to reconstruct the copper-tin diagram or to complete the ternary equilibrium diagram; but I have tried to show the necessity of reconstructing the copper-tin diagram as evident from certain experimental facts recorded in this research, and to suggest how further work can best be carried out. The solution of the ternary diagram must await the corrections to be made on the copper-tin diagram.

To Dr. Campbell under whose direction the research was begun, to Dr. Hanemann in whose laboratory it was carried out, and to Dr. Guertler who has taken a lively interest in the work throughout, I wish to express my sincere thanks and appreciation.

I, Samuel L. Hoyt, was born in Minneapolis, Minn., May 29, 1888. Graduated from the Minneapolis Central High School in 1905, and entered the State University at Minneapolis in the School of Mines. Graduated from the School of Mines in the class of 1909 receiving the degree of E. M. Studied the two years following, 1909—10 and 1910—11 at Columbia University, in the City of New York. This work was residence work for the degree of Ph. D. The two following years were spent at the Royal School of Technology, Charlottenburg, Germany, at which place the dissertation was completed. In August, 1913, become Assistant Professor of Metallography at the School of Mines, University of Minnesota, which place has been held to date.

Instruction was received from the following:

At Minneapolis; Appleby, Christianson, and Pease.

At Columbia; Walker, Campbell, Kemp, Berkey, Morgan, Munroe, and Kern.

At Charlottenburg; Hanemann, Guertler, Heyn, Bauer, Nernst, Martens, Memmler.

**PUBLISHED PAPERS:**

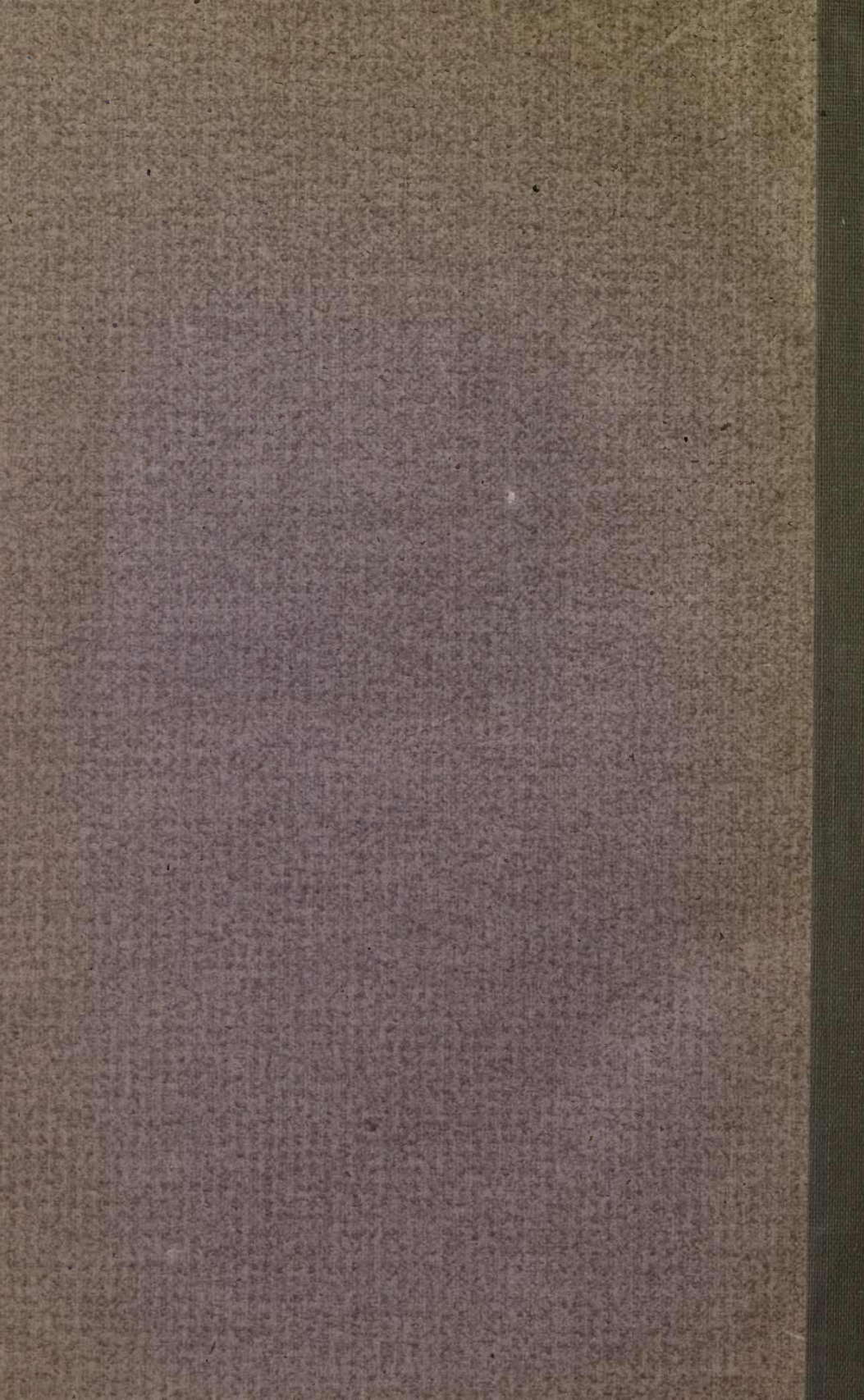
On the Copper Rich Kalchoids.

Journal of the Institute of Metals, Vol. X, 1913, No. 2.

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